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Metallic nanoparticles in active layer for hybrid photovoltaic device applications

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ABSTRACT

In this study, Poly (3-hexylthiophene) (P3HT): [6,6]-phenyl C61-butyric (PCBM): titania (TiO_2): platinum (Pt) nanoparticles (NPs) hybrid films were prepared and used as the active layer of solar cells. The use of nano-Pt in hybrid films may increase the efficiency of solar cells because of its high carrier mobility. The polyol reduction reaction was used to synthesize inorganic Pt NPs by dissolving $H_2PtCl_6 \cdot 6H_2O$ in ethylene glycol and refluxing the solvent for several hours. Then, the prepared Pt NPs were used to prepare the solar cells. The experimental results showed that the short-circuit current density and efficiency of solar cells increased from 7.31 mA/cm^2 and 2.17% to 10.10 mA/cm^2 and 3.26%, respectively. In addition, the value of incident photon-to-electron conversion efficiency reached 55% as 0.03 wt.% Pt NPs were added into the active layer P3HT:PCBM:TiO_2.

1. Introduction

The increasing demand for renewable energy resources, especially solar power, is driving researchers to develop a low-cost and efficient photovoltaic. The devices, with flexible substrates and low-cost, are an alternative to traditional inorganic-based solar cells [1–3]. Conceptually, the formation of the bulk-heterojunction phase allows for bulk separation of photoinduced excitons and high-mobility removal of electrons through the nanophase. Poly (3-hexylthiophene) (P3HT) with a fullerene derivative, is the most commonly used p-type material in polymer photovoltaics i.e. [6,6]-phenyl C61-butyric acid methyl ester (PCBM), as an electron acceptor [4–6]. Various hybrid polymer photovoltaic cells have been reported using various metal compounds, such as CdSe, PbS, TiO_2, PbSe, $CuInS_2$, etc. [7–12].

Although significant progress has been achieved, with several reported polymer solar cell devices providing power conversion efficiencies of 3%–6%, there is room for improvement. If hybrid polymer solar cells are to exhibit high-power conversion efficiencies, their carrier mobility must be improved. Blending the metal nanoparticles (NPs) into an active layer may effectively improve the carrier mobility. There are innumerable techniques available to construct metal NPs. In the past few decades, various methods were developed to synthesize polymer-stabilized NPs, such as those of Ag, Au, and Pt, which are promising materials for use in hybrid polymer solar cells [13–16]. Although there are many methods available for preparing metal NPs, applying NPs to solar cells to control their agglomeration and aggregation is problematic. A high dispersion of NPs in the active layer improves carrier mobility and results in power conversion efficiency.

A hybrid polymer fullerene inorganic metal NP photovoltaic device is fabricated by blending Pt metal NPs in the active layer. The polymer, P3HT, is an electron donor, and fullerene [6,6]-phenyl C61-butyric acid butyl ester, is an electron acceptor. Monodispersed colloidal titania (TiO_2), with a surface OH group and Pt, was used as the inorganic metal NP to improve the carrier mobility. The colloidal TiO_2 and Pt solution was prepared by using the sol–gel procedure and polyol reduction reaction, respectively. The properties of NPs and the fracture surfaces of hybrid films were examined by scanning electron microscope (SEM), transmission electron microscope (TEM), and atomic force microscope (AFM). The optical properties of hybrid films were analyzed by ultraviolet–visible (UV–vis) spectophotometer and photoluminescence (PL). Finally, the prepared P3HT: PCBM: TiO_2: Pt was then applied to fabricate the hybrid solar cell with a structure of Al/Ca/P3HT: PCBM: TiO_2: Pt/Poly(3,4-ethylenedioxythiophene): Poly(styrenesulfonate) (PEDOT: PSS)/Indium tin oxide (ITO). The optimum Pt content and operating conditions for fabricating a hybrid solar cell were also investigated.

2. Experimental details

2.1. Materials

The regioregular P3HT (RR P3HT, Aldrich, 99.995%) and PCBM-61 (Rieke Metals, Inc.) were used as the p-type semiconducting polymer and n-type semiconductor, respectively. Poly(3,4-ethylene-dioxy -thiophene):poly (styrene sulfonate) (PEDOT: PSS, Baytron

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P-VP AI4083) and Dimethyl sufoxide (DMSO, Riedel-De Haën, ≥99.5%) was used as the hole transport material and solvent, respectively. The chlorobenzene (Aldrich, 99.8%) and Chloroplatinic acid ($H_2Pt Cl_6 \cdot 6H_2O$, Show) were used to synthesize Pt colloids. In a typical reaction, $H_2PtCl_6 \cdot 6H_2O$ was dissolved in ethylene glycol (Show, 99.5%). Tetrabutoxyltitanium (Aldrich, 99%) and hydrochloric acid and n-butanol (Acros, 99.5%) was used to prepare colloidal TiO_2.

2.2. Preparation of colloidal TiO_2 and Pt NPs

The colloidal TiO_2 with OH-group on their surface were prepared by controlled sol–gel procedure. A detailed description of the procedure could be found in the literature [17]. In a typical synthesis, 6 g of tetrabutoxyltitanium, 0.3085 g HCl, 0.2 g of de-ionized water, and a desired amount of butanol were mixed at room temperature under agitation. On the other hand, Pt NPs were prepared by polyol method. In a typical synthesis, 5 ml of ethylene glycol was added into 10 ml of water, followed by an addition of 0.1 g $H_2PtCl_{6,}$ and refluxing was performed at 80 °C with vigorous stirring for 4 h. Then, the solution was placed into the rotary evaporation in which the Pt is recovered from the H_2O fraction.

2.3. Preparation of Al/Ca/P3HT:PCBM:TiO_2:Pt/PEDOT:PSS/ITO hybrid solar cell

The hybrid solar cell devices were fabricated by a spin-coating process. All films were deposited onto commercially patterned ITO (approximately 10 Ω/sq, thin-film devices) substrates after 5 min of ultrasonic cleaning in acetone followed by isopropyl alcohol. Substrates were O_2 plasma cleaned immediately prior to hole transport layer deposition in 106.66 Pa. Conductive grade PEDOT: PSS was then mixed with an organic solvent, DMSO. The PEDOT: PSS was spin coated at 1000 rpm and dried for 20 min at 150 °C. An active film was prepared composed of a P3HT and PCBM ratio 1:1, dissolved in chlorobenzene, and stirred for 12 h. A desired amount of TiO_2 and of Pt colloids was added into the P3HT: PCBM solution and stirred for 12 h. The product was labeled PCTPtX (where X represents the wt.% of Pt). Then, the active layer was prepared by spin coating at 1000 rpm on the PEDOT: PSS layer and then annealing at 150 °C for 20 min. The cathode was made by thermally depositing a Ca layer with a thickness of 60 nm and then depositing an aluminum layer with a thickness of 80 nm in a vacuum of 1.33×10^{-4} Pa. The area of the device was 0.2 cm^2.

2.4. Characterization

The fracture surfaces of the hybrid thin films were examined on a Hitachi H-2400 SEM at the voltage of 10 kV. The TiO_2 particle sizes were measured by a Hitachi H-7100 TEM at the voltage of 120 kV. A Veeco DI3100 AFM was used to probe the surface morphology of the coated films with a monolithic silicon probe under tapping mode. The tip of probe is shaped like a polygon based pyramid with a height of 10–15 μm. The baseline noise was less than 0.1 nm. The PL spectra were obtained using a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer with a 450 nm excitation wavelength. The UV–vis absorption spectrum was recorded using a Jasco Model V-650 UV–vis–NIR spectrophotometer. Performance of PV cells was measured using a calibrated AM1.5G solar simulator (Oriel 300 W) at 100 mW/cm^2 light intensity adjusted with a standard PV reference cell (monocrystalline silicon solar cell, calibrated at NREL, CO, USA). Current density–voltage (J–V) curves were recorded using MFS-PV-Basic. All fabrication steps and characterizations were performed in an ambient atmosphere. The thickness of the thin films was measured using a KLA Tencor alpha-step IQ surface profilometer with an accuracy of 71 nm. The incident photon-to-current conversion efficiency (IPCE) spectra were recorded by illuminating the samples with a 300 W Xenon lamp, dispersed by a Dongwoo-optron (South Korea) DM151i single-grating monochromator. The hybrid photovoltaic cell properties were compared with a pristine P3HT: PCBM system and the effects of the TiO_2 addition on the performance of the hybrid photovoltaic cells were studied. The crystalline structure of the active layer was analyzed using X-ray diffraction (XRD, PANalytical X'Pet PRO MPO) with Cu K_α radiation, $\lambda = 1.54056$ Å and a step size of 0.017°.

Thermogravimetric analysis (TGA) and differential scanning calormetry (DSC) were performed under a nitrogen flow using a DuPont Model 951 TGA and a DuPont Model 910S DSC at a heating rate of 20 °C/min and 10 °C/min, respectively. The TGA and DSC samples were prepared by spin coating the precursor solution on a glass substrate, followed by curing at various temperature steps as described in the film preparation. Impedance spectroscopy was measured by an impedance analyzer (CHI6143D) with an AC signal of 0.5 V in the frequency range of 0.05–100 MHz.

3. Results and discussion

Fig. 1 shows the TEM images of the synthesized Pt NPs. Fig. 1(a) shows that the Pt NPs, with a very uniform particle size of 3–4 nm, were well dispersed in the solution. Highly dispersed Pt NPs with larger surface areas have advantages in carrier mobility and cell performance. The high-resolution image of Pt NPs in Fig. 1(b) shows the oriented and ordered lattice fringes for the Pt NPs. The ring-like selected-area electron diffraction pattern indicates that the as-synthesized Pt NPs are polycrystalline structures and the d-spacing value of 0.23 nm coincides with that of face-centered-cubic (fcc) Pt (111). The phase structures of the samples were examined by XRD measurements. Fig. 2 shows the XRD patterns of powder Pt. The strong diffraction peaks at $2\theta = 39.7°$, 46.3°, and 67.9° are in agreement with the (111), (200), and (220) crystal planes of pure Pt with fcc phase (JCPDS 87-0647) [14]. Fig. 3 shows the TEM images of the hybrid PCTPt films obtained with various Pt content (0.02 wt %-0.05 wt %). Fig. 3(a)–(b) shows that the Pt NPs were well dispersed in the hybrid films when the Pt content was lower than 0.03 wt.%. When the Pt content was higher than 0.04 wt.%, the Pt

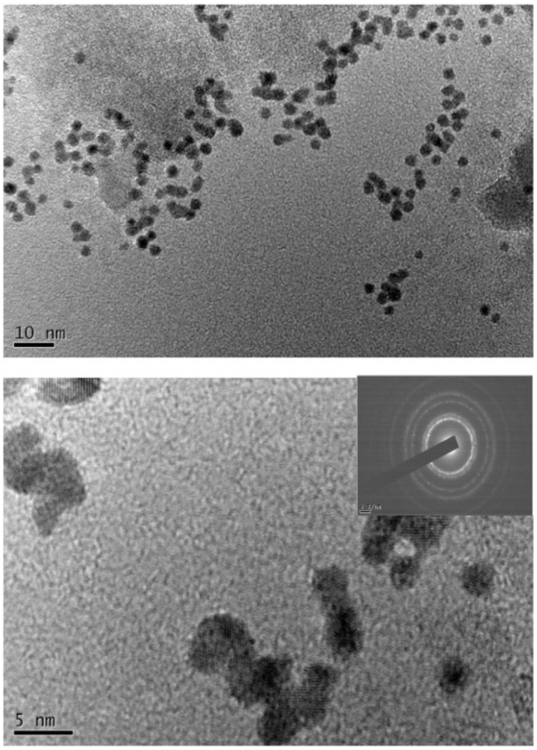

Fig. 1. TEM images of the synthesized Pt NPs.